

How to quantify structural anomalies in fluids ?

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(Dated: June 3, 2014)

Some fluids are known to behave anomalously. The so-called structural anomaly which means that the fluid becomes less structured under isothermal compression is among the most frequently discussed ones. Several methods for quantifying the degree of structural order are described in the literature and are used for calculating the regions of structural anomalies. It is implied that all of the structural order determinations yield qualitatively identical results. However, no explicit comparison was made. This paper presents such a comparison for the first time. The results of some definitions are shown to contradict the intuitive notion of a fluid. On the basis of this comparison we show that the structural anomaly can be most reliably determined from the behavior of the excess entropy.

PACS numbers: 61.20.Gy, 61.20.Ne, 64.60.Kw

I. INTRODUCTION

It is well known that some liquids demonstrate anomalous properties [1]. The most common example of an anomalous liquid is water [2]. Water has a region of density - temperature parameters where the diffusion coefficient increases with density (diffusion anomaly), thermal expansion coefficient has a negative sign (density anomaly) and the liquid becomes less structured with increasing density (structural anomaly). Another common example of an anomalous liquid is silica which also has regions of anomalous diffusion, density and structure [3]. Having analyzed a wide set of data, Errington and Debenedetti came to the conclusion that regions of different anomalies form nested domains [5]. In particular, it was shown that in the case of water, the order of anomalies is as follows: the region of anomalous density is inside the diffusion anomaly region and both of them are inside the region of the structural anomaly. In the case of silica, the order of the anomalies is different: the density anomaly is inside the structural anomaly and both of them are inside the diffusion anomaly [3]. Later on it was shown that the order of the density anomaly and the structural anomaly determined by the anomaly of excess entropy is strictly defined by the thermodynamic relations [6], while there is no such relation between the diffusion anomaly region and the other anomalies [17]. So, the diffusion anomaly can take any place in the $\rho - T$ plane with respect to other anomalies [17–19].

Among the systems which demonstrate an anomalous behavior, the simplest ones to study are the so called core-softened systems (see, for example, [7–40]). Many

core-softened systems demonstrate an anomalous behavior due to the presence of two length scales in the interaction potential. As a result, two locally preferred structures are possible: low and high density ones. The competition between these structures leads to the appearance of anomalous behavior. Later on it was shown that even some models with one scale can behave anomalously [41]. Here, anomalous behavior is related to the shape of the force as a function of distance.

It is widely believed that in the core-softened systems the hierarchy of anomalies is of the water-like type. However, recently it has been shown that the order of the region of anomalous diffusion and the regions of density and structural anomalies may be inverted depending on the parameters of the potential and may have the silica-like or some other sequences [17–19]. Several definitions of structural anomaly are available in the literature. Some of the definitions directly refer to the structural properties. They rely on different structure-dependent parameters which are usually called the order parameters (do not confuse with the order parameters in the theory of phase transitions) [5, 25, 26]. One expects that in ordinary systems the order parameter increases with density along the isotherm. The region of densities, where the order parameter decreases under densification, will be an anomalous region.

Other definitions of the structural anomaly relate it to the excess entropy $S_{\text{ex}} = S - S_{\text{id}}$ where S is the total entropy and S_{id} is the entropy of ideal gas at the same density and temperature. Entropy defines the number of states accessible to the system. So, the less ordered the system, the larger the excess entropy. In a typical liquid the excess entropy decreases with isothermal in-

creasing of density because it becomes more ordered. In an anomalous liquid there is a region where S_{ex} increases with density.

The appearance of structural anomaly in liquids was widely discussed in the literature (see, for example, [17–26, 30, 31, 33, 35, 36]). However, different authors use different definitions for the structural anomaly. It was assumed that all of the definitions give qualitatively similar results. However, we are not aware of any verification of this assumption. The main goal of this paper is to find the most consistent way to determine the region of structural anomaly. In order to do this we calculate the structurally anomalous regions by different definitions and compare them to each other. We believe that this study will clarify the relation between different definitions of structural anomaly.

II. SYSTEM AND METHODS

We study a core-softened potential system introduced in our previous publications [17–24], namely the repulsive shoulder system (RSS) which is defined by the following interparticle potential:

$$\Phi = \varepsilon(\sigma/r)^{14} + \varepsilon \cdot [1 - \tanh(k \cdot (r - \sigma_1))] / 2, \quad (1)$$

where $k = 10$, $\sigma_1 = 1.35$. Thereafter of this paper, we use the dimensionless quantities: $\tilde{\mathbf{r}} \equiv \mathbf{r}/\sigma$, $\tilde{P} \equiv P\sigma^3/\varepsilon$, $\tilde{V} \equiv V/N\sigma^3 \equiv 1/\tilde{\rho}$. As only these reduced variables are used, we will omit the tildes.

In our previous works, we presented the phase diagram of this system [20–23] and discussed the anomalous behavior. The order of anomalies corresponding to the case of the water - density anomaly region is inside the diffusion anomaly one and both of them are inside the structural anomaly. In the later works we investigated the influence of the shape of the potential on anomalies in the system. It has been shown that if the width of the repulsive shoulder increases (i.e. increases σ_1), the anomalies start to disappear. At $\sigma_1 = 1.55$, the diffusion anomaly vanishes. If $\sigma_1 = 1.8$, the density anomaly also vanished and only the structural anomaly preserves [18, 21].

While increase of the repulsion depresses anomalies, the attractive forces stabilize them [17, 19]. If the attractive well is added to the potential (1), the anomalous regions will extend to higher temperatures. Moreover, the sequence of regions changes, and at some attractive well depth the order of anomalies becomes silica-like [17, 19].

In the present work we simulated a system of 4000 particles in a cubic box in molecular dynamics. The system was simulated in the canonical ensemble - constant number of particles N , volume V and temperature T . The timestep was set at 0.005 reduced units of time. The system was equilibrated for $3 \cdot 10^6$ steps. The production

run was set at $1 \cdot 10^6$ steps. Each 500 steps the current configuration was stored in order to compute the functions of interest. The density varied from $\rho = 0.15$ up to 0.75 with the step $d\rho = 0.05$ and temperature from $T = 0.1$ up to 0.7.

All simulations in this work were done using lammmps simulation package [45].

In our previous works we defined the structural anomaly via the anomaly of the excess entropy S_{ex} . Here, since we wish to compare different definitions of the structural anomaly regions, we add some more criteria.

We compute the structural anomaly via the pair entropy

$$s_2 = -2\pi\rho \int (g(r) \cdot \ln(g(r)) - g(r) + 1) \cdot r^2 dr, \quad (2)$$

The pair entropy can be used not only for characterizing anomalous properties of a liquid [42] but also as the "one-phase" criterion of freezing [43, 44].

The translational order can be measured with the use of the order parameter τ introduced by Truskett et al. [4] and modified for water by Errington and Debenedetti [5]:

$$\tau = \frac{1}{\xi_c} \int_0^{\xi_c} |g(\xi) - 1| d\xi, \quad (3)$$

where $\xi = r \cdot \rho^{1/3}$ is the interparticle separation scaled by the mean interparticle distance, $g(\xi)$ is the radial distribution function and ξ_c is a scaled cutoff distance. In this work, we use $\xi_c = \rho^{1/3}L/2$, where $L = V^{1/3}$.

Other parameters considered here are associated with the orientational local order. To define the local orientational properties of the repulsive shoulder system we use the bond order parameter method, which has been widely used in the context of condensed matter physics [46–52], hard sphere systems [53–57], complex (dusty) plasmas [58–62], colloidal suspensions [63–65], etc.

According to this method the rotational invariants (RIs) of the rank l of both the second $q_l(i)$ and the third $w_l(i)$ orders are calculated for each particle i in the system from the vectors (bonds) connecting its center with the centers of its $N_{\text{nn}}(i)$ nearest neighboring particles:

$$q_l(i) = \left(\frac{4\pi}{(2l+1)} \sum_{m=-l}^{m=l} |q_{lm}(i)|^2 \right)^{1/2} \quad (4)$$

$$w_l(i) = \sum_{\substack{m_1, m_2, m_3 \\ m_1 + m_2 + m_3 = 0}} \begin{bmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{bmatrix} q_{lm_1}(i) q_{lm_2}(i) q_{lm_3}(i), \quad (5)$$

where $q_{lm}(i) = N_{\text{nn}}(i)^{-1} \sum_{j=1}^{N_{\text{nn}}(i)} Y_{lm}(\mathbf{r}_{ij})$, Y_{lm} are the spherical harmonics and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ are the vectors connecting the centers of particle i and j .

In Eq.(5), $\begin{bmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{bmatrix}$ are the Wigner $3j$ -symbols, and the summation in the latter expression is performed over all of the indexes $m_i = -l, \dots, l$ satisfying the condition $m_1 + m_2 + m_3 = 0$. Here, for detecting close packed crystalline structures, we calculate the rotational invariants q_4 , q_6 , w_4 and w_6 for each particle using the fixed number of nearest neighbors $N_{nn} = 12$. Particles whose coordinates in the 4-dimensional space (q_4, q_6, w_4, w_6) are sufficiently close to those of the ideal face-centered cubic (fcc), hexagonal close packed (hcp), icosahedral (ico), etc lattice are counted as fcc-like (hcp-like, ico-like) particles. By calculating the bond order parameters, it is easy to identify the disordered (liquid-like) phase (for instance, such particles have the mean bond order parameter $q_6^{\text{liq}} \simeq N_{nn}^{-1/2} \simeq 0.29 \ll q_6^{\text{fcc/hcp/ico}}$, where $N_{nn} = 12$). By varying the number of nearest neighbors N_{nn} and the rank l of bond order parameter, it is possible to identify the lattice type, quasicrystalline order, distorted hcp/fcc/ico modifications, liquid-like particles, etc. The values of q_l and w_l for some crystals are presented in Table I. Comparing the calculated values of the corresponding q_l and w_l with their ideal values we can estimate the local order in the liquid.

TABLE I: Rotational invariants q_l and w_l ($l = 4, 6$) of a few perfect crystals calculated via the fixed number of nearest neighbors (NN): hexagonal close-packed (hcp), face centered cubic (fcc), face centered tetragonal (fct), icosahedron (ico), body-centered cubic (bcc), simple hexagonal (sh), simple cubic (sc) and diamond (dia).

| c rystalline structure | q_4 | q_6 | w_4 | w_6 |
|------------------------|----------------------|-------|--------|--------|
| hcp (12 NN) | 0.097 | 0.485 | 0.134 | -0.012 |
| fcc (12 NN) | 0.19 | 0.575 | -0.159 | -0.013 |
| fct (12 NN) | 0.225 | 0.51 | 0.11 | 0.018 |
| ico (12 NN) | 1.4×10^{-4} | 0.663 | -0.159 | -0.169 |
| bcc (8 NN) | 0.5 | 0.628 | -0.159 | 0.013 |
| bcc (14 NN) | 0.036 | 0.51 | 0.159 | 0.013 |
| sh (8 NN) | 0.53 | 0.5 | 0.134 | 0.0475 |
| sc (6 NN) | 0.76 | 0.35 | 0.159 | 0.013 |
| dia (4 NN) | 0.51 | 0.628 | -0.159 | 0.013 |

To quantify the global orientational order, it is convenient to use the metrics associated with the cumulative distributions of the normalized probability distribution functions (PDF) $P(q_l)$ and $P(w_l)$ for different order parameters q_l and w_l [56, 61, 66, 67]. For instance, the cumulative function C_q^l of $P(q_l)$ is defined from:

$$C_q^l(x) \equiv \int_{-\infty}^x P(q_l) dq_l \quad (6)$$

Evidently, $C_q^l(x)$ is the abundance of particles, having $q_l < x$ and $C_q^l(\infty) \equiv 1$. The relevant order parameter Q_l^c is the position of the half-height of the cumulative

distribution C_q^l , so that $C_q^l(Q_l^c) \equiv 1/2$. Here, we use the cumulants Q_6^c and W_6^c associated with the particle distributions over bond order parameters q_6 and w_6 , respectively as indicators of the structural anomaly.

Having defined the order parameters one can determine the region of structural anomaly with respect to these parameters. It is intuitively clear from the term "order parameter" that the larger value of the order parameter corresponds to the larger structural order. Therefore, in normal fluids the order parameters should increase with increasing density along the isotherm, and if one finds a region of the isotherm where the order parameter decreases, this region will be structurally anomalous.

The opposite situation is observed in the case of excess entropy. The excess entropy decreases in case of a normal liquid, so the anomalous region is defined as the region where S_{ex} increases.

III. RESULTS AND DISCUSSION

In order to study the region of structural anomaly defined by different quantities, first of all, we need to recall the phase diagram of the system which is shown in Fig. 1(top panel). This phase diagram was already published in our previous papers. We show it here again for the sake of completeness. In the inset, the radial distribution function $g(r)$ and the number of particles $N(< r)$ in the spherical volume of radius r , at $T = 0.1$ are shown for the set of densities.

First we consider the orientational order parameters Q_6^c and W_6^c . In this study we use the fixed number of nearest neighbors $N_{nn} = 12$ for calculating the bond order parameters q_l and w_l (and their cumulative measures Q_6^c , W_6^c as well). As is clearly seen from the cumulative distributions $N(< r)$ plotted in Fig 1, in the considered density range $\rho = 0.2 \div 0.75$ the first (at low values $\rho < 0.5$) and both first and second shells (at $\rho > 0.6$), the mean number of particles is close to 12. So, the parameters q_l and w_l reflect the orientational ordering of the RSS system; according to the definition, these parameters include many body correlations (which depend on N_{nn}). It is intuitively clear that the orientational bond order parameters are much more sensitive to the local structure rearrangement at the RSS densification than the metrics which are based on the two-point correlations properties only ($g(r)$, τ , s_2).

Fig. 2 shows the parameters Q_6^c and W_6^c for a set of isotherms. One can see that they behave in opposite ways: while Q_6^c increases in the normal regime and decreases in anomalous one, W_6^c normally decreases and increases in the anomalous region. The points of extrema of these parameters almost coincide. However, a small difference still takes place. If these points are placed in the phase diagram, the anomalous region will extend to the

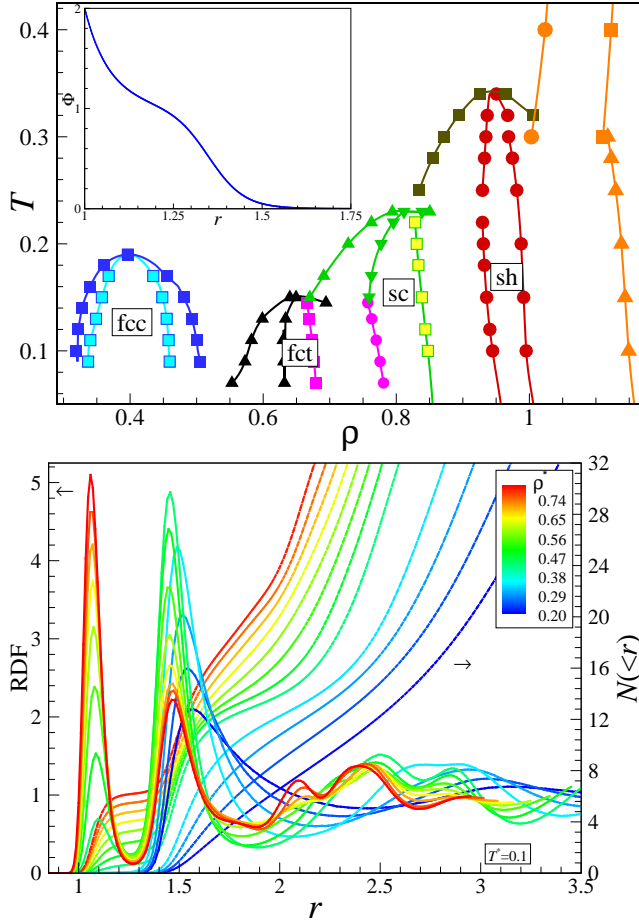


FIG. 1: (Color online). Top panel: Phase diagram of the repulsive shoulder system (RSS) with potential (1). Domains of different crystalline order (face-centered cubic (fcc), face-centered tetragonal (fct)), simple cubic (sc) and simple hexagonal (sh)) are indicated. The inset shows the inter-atomic potential (Eq. 1). Bottom panel: the radial distribution function $g(r)$ and its cumulative functions $N(<r)$: ($N(<r) \equiv 4\pi\rho \int_0^r r'^2 g(r') dr'$) is the mean number of particles inside the sphere of radius r) at different densities ρ ; the curves are color-coded depending on the ρ value. The RSS dimensionless temperature $T = 0.1$.

right above the crystal phases. Intuitively, the anomalies can be explained the influence of the soft core of the potential. However, at the densities of the minima of Q_6^c or maxima of W_6^c , the influence of the soft core must be relatively small. So, these orientational parameters do not fit the intuitive expectations.

In order to elucidate this point, it was proposed to determine the left-hand branch (low densities) of the region of structural anomaly is through the orientational order parameter Q_6^c while the right-hand branch (high densities), by the translational parameter τ [5]. However, it looks to be nonselfconsistent: if we define the structural anomaly as an anomaly in some parameter it should be expected that the same parameter gives the

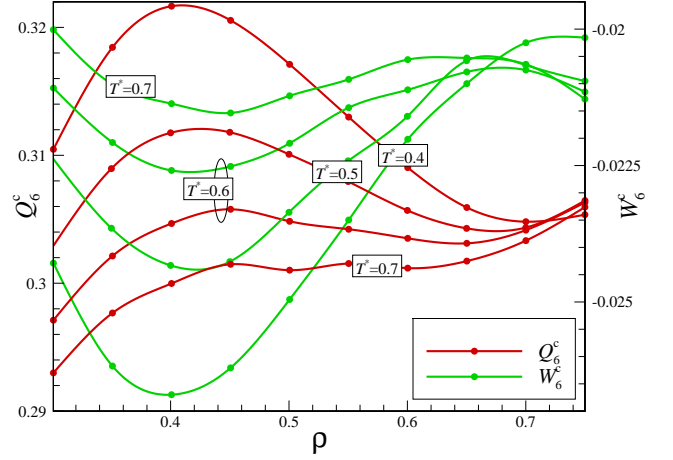


FIG. 2: (Color online). Orientational order parameters associated with the cumulative functions (see text for details) of the PDF of Q_6^c (red lines) and W_6^c (green lines) calculated by using $N_{nn} = 12$ versus RSS dimensionless density ρ at different temperatures T (indicated on the plot).

whole anomalous region.

The region of structural anomaly can be defined through the minima and maxima of the translational order parameter τ , as it was done, for example, in Refs. [25, 26]. Fig. 3 shows the translational order parameter τ along a set of isotherms. One can see that at low enough temperatures it demonstrates the maximum and minimum; so there is a region of anomalous behavior of this parameter. If one takes the points of maxima and minima of τ one can see that as the temperature increases the anomalous region goes to the left, i.e. toward the lower densities. Moreover, the maximum temperature of this anomaly is rather high - $T_{\max} = 0.6$. Intuitively one relates the presence of anomalous behavior to the presence of two length scales in the potential. In particular, two scales lead to the formation of the low-density FCC phase in the phase diagram (Fig. 1). But the τ anomaly (as well as the q_6 and w_6 anomalies) exists at quite high temperatures when the two scales do not play so important role. So, this order parameter also seems to contradict to our intuitive expectations.

Next we consider the definition of the structural anomaly by the excess entropy S_{ex} and the pair contribution to the excess entropy s_2 . It is commonly supposed that the pair entropy is a good approximation to the excess entropy. Usually it is referred to the Lennard-Jones system [68] where the pair entropy accounts for approximately 80 – 85 percent of the total excess entropy. However, as it was shown in our previous publication, in the case of core-softened systems s_2 strongly deviates from the total excess entropy [22]. Fig. 4 compares the total excess entropy with the pair entropy at a relatively high temperature ($T = 0.7$ which is higher then the anomalous region) and at a low temperature ($T = 0.2$). One can

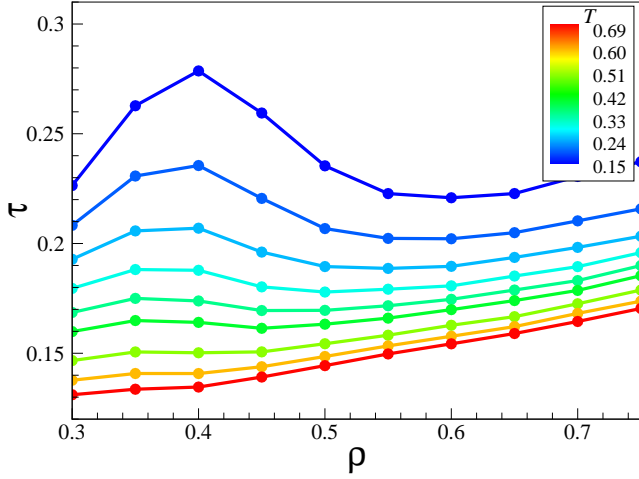


FIG. 3: (Color online). Translational order parameter τ along the following isotherms (from bottom to top): 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.5, 0.6, 0.7.

see that the difference between the two curves is rather large. For $T = 0.7$ it reaches 40%. At low temperatures the largest difference is approximately 75% at $\rho = 0.4$. At the same time, at high densities under $T = 0.2$ the pair entropy very closely follows the S_{ex} curve. One can conclude that s_2 can be close to the total excess entropy but its real location with respect to S_{ex} is rather unpredictable. So, it is not a good quantity to refer to. However, since s_2 is actively studied in the literature we also computed it and found the structural anomaly region related to s_2 . The corresponding curve is shown in Fig. 5 where all definitions of the structural anomaly are shown for comparison.

Typically radial distribution function is used for characterizing the structure of liquid. The translational order parameter τ and the pair excess entropy s_2 represent two different ways to quantify this structure. However, one can see that these two ways give very different results which clearly indicates that a solid theoretical basis is needed for quantifying the liquid structure by radial distribution function derivatives.

Finally we determined the structural anomaly through the maxima and minima of S_{ex} as it was done in our previous publications [17–23]. The resulting curve is shown in Fig. 5.

It is seen from Fig. 5 that all regions differ widely. This leads to an obvious conclusion that if someone meets “a structural anomaly” in the literature one should mention with respect to which quantity this anomaly is defined. However, to date this question was not clarified. As a result the confusion is possible. For example, it is common in the literature to define the “water like order of anomalies” (density anomaly is inside the diffusion anomaly and both of them are inside the structural anomaly) and the “silica-like order” (density anomaly is inside the struc-

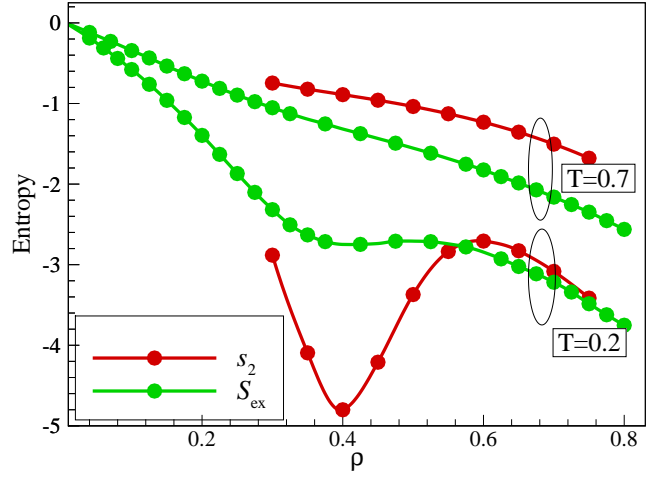


FIG. 4: (Color online). Comparison of total the excess entropy S_{ex} and the pair entropy s_2 at $T = 0.7$ and $T = 0.2$. The ovals unite the curves corresponding to the same temperature.

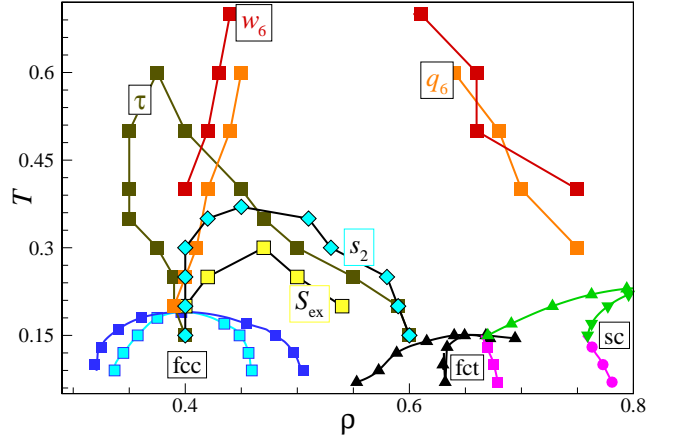


FIG. 5: (Color online). The regions of structural anomalies corresponding to all of the all definitions described in the text, placed in the phase diagram. The curves of q_6 and w_6 are cut at the top since they go into very high temperatures which are beyond the interest of the present study.

tural anomaly and both of them are inside the diffusion anomaly). However, if one considers, for example, Fig. 11 (d) of Ref. [71] where the anomalous regions of SPC/E water are shown one can see that the region of anomalous s_2 is located inside the anomalous diffusion region. Another region of the structural anomaly is defined in Ref. [71] by the local tetrahedral order parameter q_{tet} associated with the atom i is defined as

$$q_{\text{tet}} = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 (\cos \psi_{jk} + 1/3)^2, \quad (7)$$

where ψ_{jk} is the angle between the bond vectors \mathbf{r}_{ij} and \mathbf{r}_{ik} , where j and k label the four nearest neighbor atoms of the same type[6]. q_{tet} characterizes the orientational

order and in this sense is close to Q_6^c . This region covers the diffusion anomaly. It means that depending on the definition of the structural anomaly, one can observe in SPC/E water or water-like or silica-like behavior. Thinking about this problem one finds very unusual to observe the silica-like behavior of water. Apparently, it is necessary to use unambiguous definitions.

In order to decide which definition of the structural anomaly is the most adequate, we propose to use the following reasoning.

As it was shown in Ref. [6] (see also [17–19]), there are some thermodynamic relations between the regions of anomalous density and the excess entropy (note, that in Ref. [6] similar relation was erroneously established for the diffusion anomaly region [22].) If the derivative of S_{ex} with respect to the logarithm of density is considered

$$\frac{\partial S_{\text{ex}}}{\partial \ln(\rho)} > c, \quad (8)$$

$c = 0$ will correspond to the structural anomaly defined through excess entropy, while $c = 1$ is the condition for the density anomaly [6]. It means that the region of anomalous density is always inside the region of anomalous excess entropy. So, the thermodynamically consistent relation between the regions of two anomalies is established. Note, that in the considered set of anomalies (density, structure and diffusion), two of them are defined via thermodynamic properties (density and structure via S_{ex}), and diffusion has the dynamic nature. The alternative definitions via the order parameters are not thermodynamically consistent and have the structural nature. As a result, they do not obey any relations like Eq. (8) which makes them less convenient to analyze the relation between the anomalies. It is worth to emphasize that the derivation of Eq. (8) is purely thermodynamical and does not contain any reference to a concrete potential. This relation between the excess entropy anomaly and the density anomaly is based on the exact thermodynamic relations, so it is valid for any system. Similar relation for the diffusion anomaly which was proposed in Ref. [6] was based on the Rosenfeld scaling relations between the diffusion coefficient and the excess entropy [69, 70]. However, as it was shown later [22], the Rosenfeld relation breaks down in anomalous regions and, therefore, it cannot be used for identifying the relative location of the regions of density, structure and diffusion anomalies.

Although the orientational order parameters Q_6^c and W_6^c are the most powerful tool for quantifying the structure, there are some difficulties in applying these metrics to fluids. The most important problem is a correct definition of the nearest neighbors in liquid. Although the determination of the nearest neighbor of a particle is of great importance there is no unique definition in the literature. Several definitions are available in the literature [49, 72–74] and the application of different definitions can alter the results, especially in the region of anomalies

where the presence of two scales in the potential is most important. Although the number of nearest neighbors in liquid depends on density and temperature, we believe that using the fixed number of nearest neighbors gives qualitatively correct results.

So, our point of view is that the definition of the structural anomaly via S_{ex} is the most adequate at least for two reasons: (i) only this definition has the well-defined thermodynamic meaning, and (ii) there is a strict thermodynamic relation between the density anomaly and the excess entropy anomaly.

IV. CONCLUSIONS

The present paper discusses different definitions of the structural anomaly in fluids, which one can find in literature, on the basis of the core-softened potential, introduced in our previous papers [17–24]. We calculate the regions of structural anomalies with the use of different definitions and compare them with each other. We show that depending on the definition these regions can look rather different. In our opinion, the most consistent definition of the structural anomaly in fluids is the one, based on the behavior of the excess entropy, because only this definition has the well-defined thermodynamic meaning. The other definitions can be also used depending on the physical sense of the problem and convenience of calculations; however, it is always necessary to remember that different definitions can lead to drastically different results.

Yu.F. and E.T. thank the Russian Scientific Center Kurchatov Institute and Joint Supercomputing Center of Russian Academy of Science for computational facilities. The work was supported in part by the Russian Foundation for Basic Research (Grants No 14-02-00451, 13-02-91177, 13-02-12008, 13-02-00579, 13-02-00913 and 13-02-01099) and the Ministry of Education and Science of Russian Federation (project MK-2099.2013.2).

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